

# Computational investigation of static multipole polarizabilities and sum rules for ground-state hydrogen-like ions

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## Abstract

High precision multipole polarizabilities,  $\alpha_\ell$  for  $\ell \leq 4$  of the  $1s$  ground state of the hydrogen isoelectronic series are obtained from the Dirac equation using the B-spline method with Notre Dame boundary conditions. Compact analytic expressions for the polarizabilities as a function of  $Z$  with a relative accuracy of  $10^{-6}$  up to  $Z = 100$  are determined by fitting to the calculated polarizabilities. The oscillator strengths satisfy the sum rules  $\sum_i f_{0i}^{(\ell)} = 0$  for all multipoles from  $\ell = 1$  to  $\ell = 4$ . The dispersion coefficients for the long-range H-H and H-He<sup>+</sup> interactions are given.

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## I. INTRODUCTION

The present paper reports calculations of the polarizabilities of the hydrogen atom and isoelectronic ions using the Dirac equation to describe the underlying dynamics. Such calculations are now topical since some atomic polarizabilities can directly impact the definitions of two fundamental quantities, the Kelvin and the second [1]. The new generation of optical frequency standards have reached such precision that they are sensitive to the black-body radiation of the apparatus itself [2]. The resulting black-body radiation shift is largely determined by the differences in polarizabilities of the two atomic states involved in the clock transition. Additionally, very high precision measurements of the helium dielectric constant have been recently reported [3]. In conjunction with high precision calculations of the static dipole polarizability [4], these measurements can result in improved determinations of Boltzmann's constant and thus the Kelvin [3, 5].

Another reason for doing such calculations is that they can be used to verify the accuracy of computational methods and tests of fundamental theory. The polarizabilities of the hydrogenic ions are properties of the ground state of a set of systems that are often used to test the fundamental principles of physics. It is rather surprising that the first explicit calculations of the quadrupole polarizabilities of the hydrogenic ions based on the Dirac equation have only just been reported [6].

An important advance in the topic of the dipole and higher multipole polarizabilities was an investigation based on the Pauli approximation that gave expressions for the static multipole polarizabilities up to  $O(\alpha^2 Z^2)$  [7]. This was a generalization of an earlier work which gave the  $O(\alpha^2 Z^2)$  expression for the dipole polarizability [8]. The work on dipole polarizabilities was extended to  $(\alpha Z)^4$  [9],  $(\alpha Z)^6$  [10] and to all orders in terms of a generalized hypergeometric function [11]. Apart from a very recent calculation [6], the expressions for the quadrupole and higher-order polarizabilities have not had independent confirmation. There have been a number of independent calculations of the dipole polarizability and related sum rules. Many of these investigations have been computational in nature. Drake and Goldman derived expressions for some dipole oscillator strength sum rules as well as performing some explicit calculations of the dipole polarizability [12] by expanding the wave function as a linear combination of exponential type functions. Goldman [13] extended the basis set approach to calculate the dipole polarizability of hydrogenic ions from  $Z = 1$  to  $Z = 115$  using a Gauge-invariance method. A fit to the calculated polarizabilities was used to create an  $(\alpha Z)^n$  expansion of the polarizability including terms up to  $(\alpha Z)^8$ . There have been a number of other computational investigations of the dipole polarizabilities of hydrogenic ions based on Dirac equation [14–20].

The present calculations used the B-spline Galerkin method with Notre Dame (ND) boundary conditions [19]. Other approaches to the B-spline boundary conditions have been proposed [17, 18, 21–23]. There is at present no overwhelming reason for adopting more complicated boundary conditions in preference to the ND boundary conditions. The B-spline approach to atomic structure has a number of advantages [24, 25], it does not lead to linear dependence, the basis can be made effectively complete in a finite region of space, the details of the basis are easily adjustable and results are numerically stable. However, like all basis set approaches, the energy spectrum also has a sea of negative-energy states (the Dirac sea) and it is also possible for spurious states to appear in the positive energy spectrum [18]. These issues have been discussed extensively [17–19, 24].

The present B-spline calculations of the multipole polarizabilities give numerical values

that are more precise than any previous calculation. Values of associated oscillator strength sum-rules are also given. The nuclear mass was set to be infinite and the point nucleus model was adopted. Values are reported for intermediate sums including the entire set of states and also for a set of calculations that omitted the negative energy states from the Dirac Sea. Analytic expressions for the polarizabilities are constructed that are accurate to a relative precision of  $10^{-6}$  for  $Z \leq 100$ . The static multipole polarizabilities for quadrupole, octupole and hexadecupole transitions have been computed and found to be compatible with the  $O(\alpha^2 Z^2)$  expressions of Kaneko *et al* [7]. The sum rules  $\sum_i f_{0i}^{(\ell)} = 0$ , provide a valuable consistency check on the reliability of our calculations. Finally, the dispersion coefficients that describe the long-range interaction of the H-H and H-He<sup>+</sup> dimers in their ground states are presented. All results are reported in atomic units and the value of fine structure constant,  $1/\alpha = c = 137.035\ 999\ 074$  [26] was used in all calculations reported in this work unless specifically mentioned.

## II. FORMULATION

### A. Dirac equation of single-electron atomic system

The single-electron Dirac equation is

$$H_D \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (1)$$

$H_D$  is the Dirac Hamiltonian,

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(\mathbf{r}), \quad (2)$$

where  $m$  is the electron mass,  $c$  is the light velocity,  $\mathbf{p}$  is the momentum operator,  $\boldsymbol{\alpha}$  and  $\beta$  are  $4 \times 4$  matrices of the Dirac operators [7].

The wavefunction for the hydrogen-like ion can be written

$$\psi(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} iP_{n\kappa}(r)\Omega_{\kappa m}(\hat{\mathbf{r}}) \\ Q_{n\kappa}(r)\Omega_{-\kappa m}(\hat{\mathbf{r}}) \end{pmatrix}, \quad (3)$$

where  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  present the larger and small components of radial wavefunction, and  $\Omega_{\kappa m}(\hat{\mathbf{r}})$  and  $\Omega_{-\kappa m}(\hat{\mathbf{r}})$  are corresponding to the angular components. The angular quantum number  $\kappa$  are connected with  $j$  and  $\ell$ ,

$$\kappa = \ell(\ell+1) - j(j+1) - 1/4, \quad (4)$$

Substituting Eqs. (2) and (3) into Eq. (1) and separating the radial and angular components, gives the following coupled first-order differential equations for radial components  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$ ,

$$[V(r) + mc^2]P_{n\kappa}(r) + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_{n\kappa}(r) = EP_{n\kappa}(r), \quad (5)$$

$$-c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n\kappa}(r) + [V(r) - mc^2]Q_{n\kappa}(r) = EQ_{n\kappa}(r), \quad (6)$$

In this equation  $V(r)$  is the interaction potential between the electron and nucleus,

$$V(r) = -\frac{Z}{r}, \quad (7)$$

with  $Z$  being the number of nuclear charges.

In order to compare with non-relativistic calculations, we replace the energy  $E$  by  $\varepsilon = E - mc^2$ , and the radial Dirac equation can be written as matrix style,

$$\begin{pmatrix} V(r) & c(\frac{d}{dr} - \frac{\kappa}{r}) \\ -c(\frac{d}{dr} + \frac{\kappa}{r}) & -2mc^2 + V(r) \end{pmatrix} \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix} = \varepsilon \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix}. \quad (8)$$

## B. B-spline Galerkin method

The radial wavefunctions  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  are expanded in a  $N$ -dimensional basis of B-splines of order  $k$ ,

$$P(r) = \sum_{i=1}^N p_i B_i^k(r), \quad (9)$$

$$Q(r) = \sum_{i=1}^N q_i B_i^k(r), \quad (10)$$

where the subscripts  $n, \kappa$  have been omitted from the functions  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  for notational simplicity. The function  $B_i^k(r)$  only take nonzero values for the knot intervals  $t_i \leq r \leq t_{i+k}$ . The normalization condition is

$$\int_0^\infty [P^2(r) + Q^2(r)] dr = 1. \quad (11)$$

The details of the B-splines and ND boundary conditions have been discussed in detail elsewhere [18, 19]. The large and small radial components are independently expanded in a B-spline basis with the boundary conditions,  $P(R) = Q(R)$  and  $P(0) = 0$ , where  $R$  is the radius of confining cavity.

B-splines of  $k = 9$  order were used with the endpoints of multiplicity 9. An exponential knot distribution for the B-splines is adopted, e.g.

$$t_{i+k-1} = R \times \frac{\exp(\gamma(\frac{i-1}{N_1-1})) - 1}{\exp(\gamma) - 1}, \quad (12)$$

where  $i = 1, 2, \dots, N_1$  and  $N_1 = N - k + 2$  being the maximal value of  $i$ . The exponential knot parameter  $\gamma$  depends on the radius of confining cavity  $R$ ,

$$\gamma = G(Z) \times R. \quad (13)$$

The function  $G(Z)$  for  $Z \geq 2$  satisfies the recurrence relation

$$G(Z) = G(Z-1) + \frac{0.055}{Z}, \quad (14)$$

where  $G(1) = 0.055$  is an optimized value for the hydrogen atom. The confining cavity radius  $R$  (which is different for different  $Z$ ) was chosen to reproduce the exact ground-state energy [27] of the hydrogen-like ions to at least 20 significant digits

$$\varepsilon_n^{\text{Exact}} = c^2 \left[ 1 + \frac{(\alpha Z)^2}{[n - |\kappa| + \sqrt{\kappa^2 - (\alpha Z)^2}]^2} \right]^{-1/2} - c^2. \quad (15)$$

where  $n$  is the main quantum number.

### C. Polarizabilities for the single-electron atoms

In a weak external electric field, the static  $2^\ell$ -pole polarizability for an atom is usually defined in terms of a sum over all intermediate states including the continuum,

$$\alpha_\ell = \sum_i \frac{f_{gi}^{(\ell)}}{(E_i - E_g)^2}. \quad (16)$$

The initial state,  $\psi_g(\mathbf{r})$ , with energy,  $E_g$ , is excluded from the summation over  $i$ . The  $2^\ell$ -pole oscillator strength  $f_{gi}^{(\ell)}$  from ground state  $g$  to excited state  $i$  is defined

$$f_{gi}^{(\ell)} = \frac{2(E_i - E_g)|\langle \psi_g(\mathbf{r}) | r^\ell \mathbf{C}^{(\ell)}(\hat{\mathbf{r}}) | \psi_i(\mathbf{r}) \rangle|^2}{(2\ell + 1)(2j_g + 1)}, \quad (17)$$

where  $j_g$  is the total angular momentum for the ground-state. The wavefunction and energy of the excited states are  $\psi_i(\mathbf{r})$  and  $E_i$ .  $\mathbf{C}^{(\ell)}(\hat{\mathbf{r}})$  is the  $\ell$ -order spherical tensor.

Using Eq. (3), the radial and angular parts of matrix element in the Eq. (17) are

$$\langle \psi_g(r) | r^\ell | \psi_i(r) \rangle = \int_0^\infty r^\ell [P_g(r)P_i(r) + Q_g(r)Q_i(r)] dr, \quad (18)$$

$$\begin{aligned} \langle \Omega_{\kappa_g}(\hat{\mathbf{r}}) | \mathbf{C}^{(\ell)} | \Omega_{\kappa_i}(\hat{\mathbf{r}}) \rangle &= (-1)^{j_g + \frac{1}{2}} \sqrt{(2j_g + 1)(2j_i + 1)} \\ &\times \begin{pmatrix} j_g & j_i & \ell \\ -1/2 & 1/2 & 0 \end{pmatrix}. \end{aligned} \quad (19)$$

Polarizabilities that are computed including both the physical states and negative energy states of the Dirac sea in Eq. (16) are denoted by  $\alpha_\ell^\pm$ . Polarizabilities that are computed by omitting the negative energy states of the Dirac Sea in Eq. (16) are denoted by  $\alpha_\ell^+$ . The states of the Dirac sea are energetically distinct from the physical states. The polarizabilities computed using the  $O(\alpha^2 Z^2)$  expressions of [7] are denoted as  $\alpha_\ell^K$ .

The polarizabilities can be expanded as a series in powers of  $(\alpha Z)^2$ . The series is written

$$\alpha_\ell^R = \alpha_\ell^{\text{NR}} \left[ 1 + \sum_{i=1}^n \lambda_{2i} (\alpha Z)^{2i} \right], \quad (20)$$

where the non-relativistic multipole polarizabilities,  $\alpha_\ell^{\text{NR}}$ , for the ground-state hydrogen-like ions, which have the exact values [28]

$$\alpha_\ell^{\text{NR}} = \frac{(2\ell + 2)!(\ell + 2)}{\ell(\ell + 1)2^{2\ell+1}Z^{2\ell+2}}. \quad (21)$$

#### D. Oscillator strength sum rules

There are a number of oscillator strength sum rules besides those which define the multipole polarizabilities. We make the definition

$$S_\ell(n) = \sum_i f_{gi}^{(\ell)} (E_i - E_g)^n. \quad (22)$$

The expression with  $\ell = 1$  and  $n = -2$  is the dipole polarizability. The case when  $\ell = 1$  and  $n = 0$  is called the Thomas-Reiche-Kuhn (TRK) sum rule. In the non-relativistic calculation,  $S_1(0)$  should be equal to the number of the electrons. The case with  $\ell = 1$  and  $n = -3$  is related to the non-adiabatic dipole polarizability [29]. One finds that  $S_1(-3) = 43/(4Z^6)$  for non-relativistic hydrogenic atoms. The  $S_1(-1)$  coefficient [30] is related to the long-range atom wall dispersion coefficient [31]. One finds that  $S_1(-1) = 2/Z^2$  for non-relativistic hydrogenic atoms. The relativistic sum rules are useful in testing the completeness of basis sets for variational representations of the Dirac spectrum [32] and set a foundation for testing other methods.

As with the polarizabilities, the sum-rules can be evaluated by summing over all states, or just the positive energy states. Sum rules that are computed including both positive and negative energy states in Eq. (22) are denoted by  $S_\ell^\pm(n)$ . Sum rules that omit the states from the negative energy sea from the sum are denoted by  $S_\ell^+(n)$ .

### III. RESULTS AND DISCUSSIONS

#### A. Polarizabilities and sum rules for hydrogen

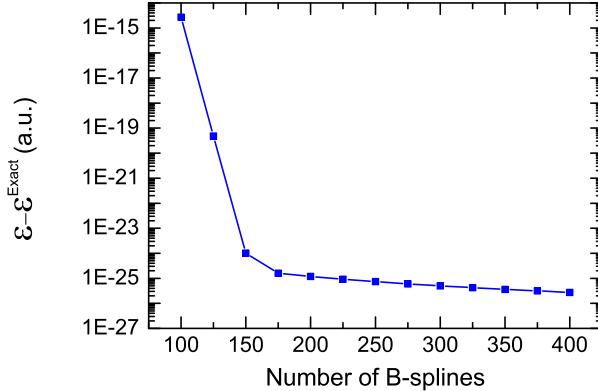


FIG. 1: (color online). The convergence of ground-state energy (a.u.) relative to the exact Dirac equation energy of the hydrogen ground state. The number of B-spline basis functions is  $N$ , while the radius of confining cavity is  $R = 400$  a.u.

The difference of the B-spline ground-state energy from the exact energy given by Eq. (15) (this is  $-0.500\ 006\ 656\ 596\ 553\ 596\ 900\ 786\ 4298$  a.u.) as a function of the dimension of the B-spline basis is plotted in Fig.1. This calculation was performed with a confinement radius of  $R = 400$  a.u.. This ensures that none of the atomic sum rules reported in this paper are

TABLE I: The convergence of the static multipole polarizabilities  $\alpha_\ell^\pm$  (units of a.u.) for the hydrogen atom ground state as the dimension,  $N$ , of the B-spline basis set was increased. The radius of the confining cavity is  $R = 400$  a.u.

$N$	$\alpha_1^\pm$	$\alpha_2^\pm$	$\alpha_3^\pm$	$\alpha_4^\pm$
100	4.499 751 495 18	14.998 829 821	131.2379	
150	4.499 751 495 177 64	14.998 829 822 856 41	131.237 821 447 83	2126.028 674 4992
200	4.499 751 495 177 639 27	14.998 829 822 856 441 76	131.237 821 447 844 63	2126.028 674 499 1281
250	4.499 751 495 177 639 267 48	14.998 829 822 856 441 70	131.237 821 447 844 661	2126.028 674 499 128 81
300	4.499 751 495 177 639 267 398	14.998 829 822 856 441 699 67	131.237 821 447 844 662 144	2126.028 674 499 128 831 0
350	4.499 751 495 177 639 267 396 1	14.998 829 822 856 441 699 61	131.237 821 447 844 662 150 7	2126.028 674 499 128 831 4
400	4.499 751 495 177 639 267 396 02	14.998 829 822 856 441 699 608	131.237 821 447 844 662 151 0	2126.028 674 499 128 831 46

TABLE II: The comparison of dipole sum rules,  $S_1^\pm(n)$  and  $S_1^+(n)$ , for the H(1s) ground state. The exact expressions of sum rule are also presented in the fourth-column with  $\gamma_1 = \sqrt{\kappa^2 - \alpha^2 Z^2}$  [12]. The ratio  $\Delta S_1(n)/S_1^{\text{exact}}(n) = [S_1^{\text{exact}}(n) - S_1^\pm(n)]/S_1^{\text{exact}}(n)$ . The non-relativistic values are in the column  $S_1^{\text{NR}}(n)$ . The value of  $S_1^\pm(0)$  is not stable and gets smaller as the B-spline basis dimension is increased. The notation  $a[b]$  means  $a \times 10^b$ .

Sum rule	$S_1^+(n)$	$S_1^\pm(n)$	$S_1^{\text{NR}}(n)$	$S_1^{\text{exact}}(n)$	$\frac{\Delta S_1(n)}{S_1^{\text{exact}}(n)}$
$S_1(-3)$	10.749 260 777 454 106 9	10.749 260 777 454 125 8	10.75		
$S_1(-2)$	4.499 751 495 886 496 76	4.499 751 495 177 639 27	4.50		
$S_1(-1)$	1.999 911 249 278 034 15	1.999 937 873 065 244 31	2.0	$\frac{(\gamma_1 + 1)(2\gamma_1 + 1)}{3Z^2}$	$7[-19]$
$S_1(0)$	0.999 955 631 350 807 45	1[-29]	1.0	$0$	$-1[-29]$
$S_1(1)$	0.666 563 210 276 996 94	3.755 773 008 441 865 7y[4]	$\frac{2}{3}$	$2/\alpha^2$	$2[-18]$
$S_1(2)$	1.298 802 722 313	-1.410 595 609 170 78[9]	$\frac{4}{3}$	$-\frac{4}{3\alpha^4} \left( \gamma_1 + \frac{2}{\gamma_1} \right)$	$7[-16]$
$S_1(3)$	—	5.298 0179 899 7[13]	—	$\frac{8}{3\alpha^6} \left[ \frac{2(\gamma_1^2 - 1)(\gamma_1 - 2)}{\gamma_1(2\gamma_1 - 1)} + 3 \right]$	$-2[-12]$

influenced by the size of the confinement radius. The energy was converged to 25 significant digits for a basis with  $N = 400$ .

Table I shows the convergence of the static multipole polarizabilities,  $\alpha_\ell^\pm$ , for the H(1s) state as the dimension of the B-spline basis was increased from  $N = 100$  to  $N = 400$ . The radius of confining cavity is  $R = 400$  a.u. The static dipole polarizability  $\alpha_1^\pm$ , is computed to a precision of 22 digits. The higher-order polarizabilities  $\alpha_2^\pm$ ,  $\alpha_3^\pm$ , and  $\alpha_4^\pm$  have not achieved the same degree of precision, but are still computed to a precision of 21, 20, and 20 effective figures respectively. The present  $\alpha_1^\pm = 4.499 751 495 177 639 267 396 02$  a.u. is  $4 \times 10^{-11}$  a.u. larger than the result  $4.499 751 495 142 92$  a.u. of Goldman [13]. This is due to the different fine structure constant used. When the fine-structure constant  $\alpha$ , is set to the value used by Goldman, namely  $1/\alpha = 137.035 999 074$ , the B-spline polarizability changed to  $\alpha_1^\pm = 4.499 751 495 142 916$  a.u. This is in perfect agreement with that of Goldman. All hydrogen atom sum-rules reported from now on use the  $N = 400$ ,  $R = 400$  a.u. B-spline basis.

Exact expressions exist for a number of the dipole sum rules given by Eq. (22). For example, the expressions for the exact non-relativistic electric-dipole sum rules  $S_1(n)$  have been derived for  $n = -5, -4, \dots, 2$  [30, 33]. The non-relativistic dipole sum-rule diverges for  $n \geq 3$ . Expressions for some dipole sum rules for the Dirac hydrogen atom have been given by Drake and Goldman [12]. The Dirac equation sum rules were derived by using closure

TABLE III: The comparison of the H(1s) static multipole polarizabilities and sum rules with and without the negative energy states. Values for  $S_\ell^\pm(0)$  are not numerically stable and tend to decrease as the basis is enlarged. The notation  $a[b]$  means  $a \times 10^b$ .

Sum rule	$S_\ell^+$	$S_\ell^\pm$	Non-relativistic
$S_2(-3)$	26.747 582 450 922 508 1	26.747 582 450 922 621 3	26.750
$S_2(-2)$	14.998 829 827 109 609 3	14.998 829 822 856 441 7	15.0
$S_2(-1)$	8.999 384 961 848 033 62	8.999 544 703 293 683 54	9.0
$S_2(0)$	5.999 605 961 023 935 20	-1[-28]	6.0
$S_2(1)$	4.799 574 122 244 155 50	2.253 393 804 665 723 66[5]	4.80
$S_2(2)$	5.598 084 401 298 530 18	-8.463 168 026 239 51[9]	5.60
$S_2(3)$	20.043 653 259 626	3.178 616 122 279 928[14]	20.80
$S_3(-3)$	204.041 400 069 326 002	204.041 400 069 327 276	204.06250
$S_3(-2)$	131.237 821 495 692 427	131.237 821 447 844 662	131.250
$S_3(-1)$	89.992 366 277 948 754 1	89.994 163 347 335 786 6	90.0
$S_3(0)$	67.494 445 945 723 638 3	6[-24]	67.50
$S_3(1)$	57.851 751 717 231 297 2	2.535 018 531 367 228 21[6]	$\frac{405}{7} = 57.8571428$
$S_3(2)$	61.704 978 988 083 113 1	-9.520 821 387 020 48[10]	$\frac{432}{7} = 61.7142857$
$S_3(3)$	100.225 824 655 056 308	3.575 836 136 347 471[15]	$\frac{702}{7} = 100.2857142$
$S_4(-3)$	3043.342 638 220 471 07	3043.342 638 220 494 85	3043.687 50
$S_4(-2)$	2126.028 675 392 279 56	2126.028 674 499 128 83	2126.25
$S_4(-1)$	1574.846 608 527 950 22	1574.880 153 465 178 52	1575.0
$S_4(0)$	1259.880 083 503 994 17	9[-19]	1260.0
$S_4(1)$	1119.885 837 666 203 30	4.731 967 094 641 248 23[7]	1120.0
$S_4(2)$	1159.848 826 903 744 95	-1.777 189 196 560 64[12]	1160.0
$S_4(3)$	1530.311 794 804 461	6.674 763 648 090 144[16]	$\frac{4591}{3} = 1530.66666666$

to sum over the complete set of positive and negative energy states and the expressions are given in Table II. The Dirac equation sum-rule for  $S_1(3)$  is convergent due to cancellations between the terms with positive and negative energies.

Table II compares the dipole sum rules of the H(1s) with and without the contributions of the states in the negative energy sea. All the digits listed are converged with respect to further enlargement of the B-spline basis. The sum-rules,  $S_1^\pm(0)$ ,  $S_1^\pm(1)$  and  $S_1^\pm(2)$ , agree with the exact expressions to better than 15 digits. Agreement is not so good for  $S_1(3)$  but in this case the sum is more sensitive to terms that occur at larger positive and negative energies. There was no evidence of convergence for  $S_1(3)$  when the states of the negative energy sea were omitted from intermediate sum. This is consistent with the non-relativistic result of Lamm and Szabo [34].

The value  $S_1^+(0)$ , which omits the states from the Dirac sea, is close to the non-relativistic value of nuclear charge  $Z = 1$ . Upon making the substitution  $\langle p^2 \rangle = Z^2$  in existing expressions [35, 36], we obtain the result

$$S_1^{+\text{Levinger}}(0) = 1 - \frac{5\alpha^2 Z^2}{6} + \dots, \quad (23)$$

Evaluating this expression for  $Z = 1$  gives,  $S_1(0) = 0.999 955 6238$ , which is only  $8 \times 10^{-9}$  different from the B-spline evaluation. The degree of difference between  $S_1^{\text{NR}}(n)$  and  $S_1^+(n)$  gets larger as  $n$  increases. The difference is 30% for  $S_1(2)$ .

The contribution that the negative-energy states make to the dipole sum rules depends on  $n$ . The negative-energy states of the Dirac sea contribute less than  $2 \times 10^{-5}$  to  $S_1^\pm(-1)$ ,  $2 \times 10^{-10}$  to  $S_1^\pm(-2)$ , and  $2 \times 10^{-15}$  to  $S_1^\pm(-3)$ . This is not surprising. The negative energy states are located at energies of order  $-2c^2$ . So the contributions of the negative energy states decrease as  $n$  in Eq. (22) becomes increasingly negative. Conversely, the differences between the  $S_1^\pm(n)$  and the  $S_1^+(n)$  sum rules can be expected to increase as  $n$  increases.

TABLE IV: The static dipole polarizabilities for the ground-state of selected hydrogen-like ions. The present values are listed in the third- and fourth-columns for two sets of  $c = 1/\alpha$ . All the tabulated digits of the present work are insensitive to further enlargement of the basis. The notation  $a[b]$  means  $a \times 10^b$ .

$Z$	$\alpha_1^+$ $c = 137.035\ 999\ 074$	$\alpha_1^\pm$ $c = 137.035\ 999\ 074$	$\alpha_1^\pm$ $c = 137.035\ 989\ 5$	$\alpha_1^\pm$ Goldman [13]
1	4.499 751 495 886 496 765 8	4.499 751 495 177 639 267 4	4.499 751 495 142 915 967 2	4.499 751 495 142 92
2	0.281 187 875 627 153 384 5	0.281 187 874 918 503 235 4	0.281 187 874 909 822 724 5	0.281 187 874 909 82
5	7.190 061 953 255 011 860[-3]	7.190 061 460 476 174 63[-3]	7.190 061 244 659 087 6[-3]	7.190 061 244 659 0[-3]
10	4.475 171 382 242 160 041[-4]	4.475 164 360 625 272 209[-4]	4.475 164 357 157 090 8[-4]	4.475 164 357 157[-4]
15	8.778 661 031 860 895 31[-5]	8.778 591 625 838 392 08[-5]	8.778 591 610 447 560 3[-5]	8.778 591 610 447[-5]
20	2.750 591 823 590 310 61[-5]	2.750 523 499 062 579 08[-5]	2.750 523 490 423 618 6[-5]	2.750 523 490 424[-5]
25	1.112 456 189 324 034 04[-5]	1.112 389 181 457 920 41[-5]	1.112 389 175 944 142 1[-5]	1.112 389 175 944[-5]
30	5.281 595 642 877 009 9[-6]	5.280 940 730 404 758 7[-6]	5.280 940 692 243 592 6[-6]	5.280 940 692 243[-6]
35	2.798 031 223 308 353 9[-6]	2.797 393 149 766 563 6[-6]	2.797 393 121 842 089 7[-6]	2.797 393 121 842[-6]
40	1.604 622 695 629 832 0[-6]	1.604 002 839 548 263 7[-6]	1.604 002 818 268 128 9[-6]	1.604 002 818 268[-6]
45	9.767 839 136 814 269[-7]	9.761 833 945 433 110[-7]	9.761 833 778 188 453 4[-7]	9.761 833 778 187[-7]
50	6.226 889 347 856 944[-7]	6.221 086 480 106 640[-7]	6.221 086 345 451 685 9[-7]	6.221 086 345 451[-7]
55	4.116 918 654 470 464[-7]	4.111 325 157 474 914[-7]	4.111 325 046 935 820 5[-7]	4.111 325 046 936[-7]
60	2.802 469 149 798 750[-7]	2.797 090 474 417 353[-7]	2.797 090 382 223 343 9[-7]	2.797 090 382 224[-7]
65	1.953 091 120 155 380[-7]	1.947 931 407 519 126[-7]	1.947 931 329 604 639 5[-7]	1.947 931 329 604[-7]
70	1.387 222 340 637 801[-7]	1.382 284 686 111 543[-7]	1.382 284 619 529 769 8[-7]	1.382 284 619 530[-7]
75	1.000 397 933 028 34[-7]	9.956 846 315 732 27[-8]	9.956 845 741 359 051 6[-8]	9.956 845 741 359[-8]
80	7.301 102 574 925 93[-8]	7.256 230 363 582 21[-8]	7.256 229 864 059 587 8[-8]	7.256 229 864 060[-8]
85	5.376 751 290 435 41[-8]	5.334 153 759 283 73[-8]	5.334 153 321 793 719 5[-8]	5.334 153 321 795[-8]
90	3.984 403 901 650 36[-8]	3.944 093 881 570 48[-8]	3.944 093 496 045 404 3[-8]	3.944 093 496 045[-8]
95	2.962 871 397 452 10[-8]	2.924 863 256 366 13[-8]	2.924 862 914 773 842 2[-8]	2.924 862 914 774[-8]
100	2.204 334 865 912 88[-8]	2.168 647 587 493 68[-8]	2.168 647 283 324 507 9[-8]	2.168 647 283 325[-8]

Table II shows that this indeed does happen. The difference between  $S_1^\pm(2)$  and  $S_1^+(2)$  is nine orders of magnitude.

Table III gives the sum rules for the higher-order multipoles for the hydrogen-atom ground state. The  $S_2(-2)$ ,  $S_3(-2)$ , and  $S_4(-2)$  are the multipole polarizabilities  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  respectively. The sum-rules,  $S_\ell^\pm(n)$ , omitting the states from the Dirac sea are within 0.1% of the non-relativistic values with the exception of  $S_2(3)$ . This is also true for the sum-rules,  $S_\ell^\pm(n)$ , with  $n < 0$  that also include the Dirac sea.

The most striking results from Table III are the  $S_\ell^\pm(0)$  sum-rules which do not exceed  $10^{-18}$ . Levinger *et al* [35] have pointed out that the Dirac Hamiltonian involves terms linear in the particle momentum  $\mathbf{p}$  and that as a consequence the Bethe sum rule for  $\exp(i\mathbf{q} \cdot \mathbf{r})$  should be identically zero. The expansion of  $\exp(i\mathbf{q} \cdot \mathbf{r})$  implicitly involves dipole, quadrupole and octupole matrix elements. Therefore, it is expected that  $S_\ell(0) = 0$  for all  $\ell$ .

The contributions of the negative-energy Dirac Sea to the  $S_\ell^\pm(n)$  sum-rules are actually greater than the contributions from the physical states for  $n \geq 1$ . They exceed the contribution from the physical states by amounts from 4 to 14 orders of magnitude.

## B. Polarizabilities for the hydrogen isoelectronic series

Table IV presents the static dipole polarizabilities for a number for hydrogen-like ions in their ground-state. All the digits listed in this table are converged with respect to further enlargement of the B-spline basis. In order to facilitate comparison of the present polarizabilities with those of Goldman [13], we repeated the calculations but used the the same speed of light  $c = 137.035\ 989\ 5$  (in atomic units) as Goldman. The agreement

with the polarizabilities of Goldman could hardly have been better. At  $Z = 10$  we got  $\alpha_1^\pm = 4.475\ 164\ 357\ 157\ 0908 \times 10^{-4}$  a.u., in agreement with all published digits of Goldman. The same is true for the polarizability at  $Z = 90$ , namely  $3.944\ 093\ 496\ 045\ 4043 \times 10^{-8}$  a.u. This level of agreement was achieved for all values of  $Z$  from 1 to 100. The only disagreements amounted to  $\pm 1$  in the last significant digit reported by Goldman [13].

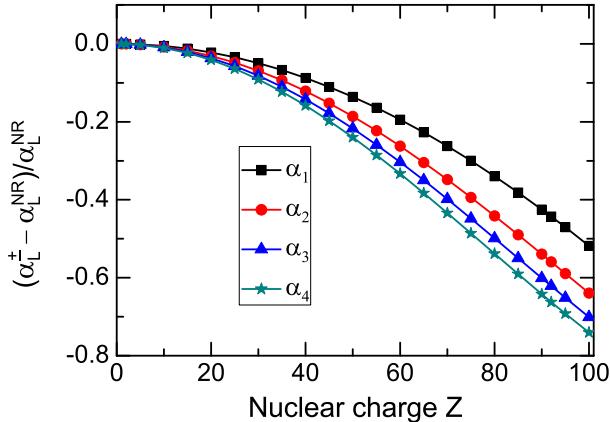


FIG. 2: (color online). The impact of relativistic effects on the multipole polarizabilities for the hydrogen isoelectronic series. The ratio  $(\alpha_\ell^\pm - \alpha_\ell^{NR})/\alpha_\ell^{NR}$  is plotted.

The higher-order polarizabilities,  $\alpha_\ell^\pm$  of the ground-states of some selected hydrogen-like ions are presented in Table V. All the reported digits are insensitive to further enlargement in the B-spline basis. Fig. 2 shows the influence of relativistic effect on multipole polarizabilities. The relativistic effect becomes larger as the nuclear charge,  $Z$ , is increased. The relative size of the relativistic effect is smallest for the dipole polarizability and largest for  $\alpha_4$ .

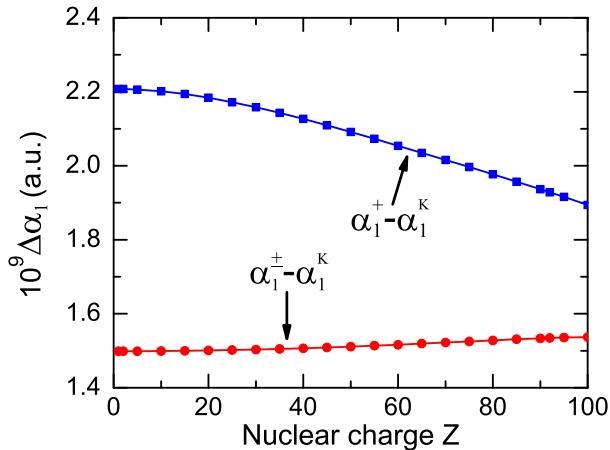


FIG. 3: (color online). Plot of  $10^9 \Delta \alpha_1/Z^2$  as a function of nuclear charge,  $Z$ .

The difference of the  $\alpha_1^\pm$  and  $\alpha_1^+$  polarizabilities from the Kaneko polarizabilities are illustrated in Fig. 3. We define  $\Delta \alpha_1^\pm = (\alpha_1^\pm - \alpha_1^K)$  with a similar relation used to define  $\Delta \alpha_1^+$ . Fig. 3 plots  $10^9 \Delta \alpha_1$  as a function of  $Z$ . These are seen to go to a constant value as

$Z \rightarrow 0$ . From Eq. (20) we deduce

$$\Delta\alpha_1^\pm = \frac{9}{2Z^4} \left[ \left( \lambda_2 + \frac{28}{27} \right) (\alpha Z)^2 + O(\alpha^4 Z^4) \right]. \quad (24)$$

This expression can only go to a constant in the  $Z \rightarrow 0$  limit when  $\lambda_2 = -\frac{28}{27}$ . Fig. 3 demonstrates that  $\alpha_1^\pm$ ,  $\alpha_1^+$ , and  $\alpha_1^K$  are equal to order  $O(\alpha^2 Z^2)$ . The different  $Z \rightarrow 0$  asymptotes for  $\Delta\alpha_1^\pm$  and  $\Delta\alpha_1^+$  indicate that the  $O(\alpha^4 Z^4)$  terms are different for  $\alpha_1^\pm$  and  $\alpha_1^+$ .

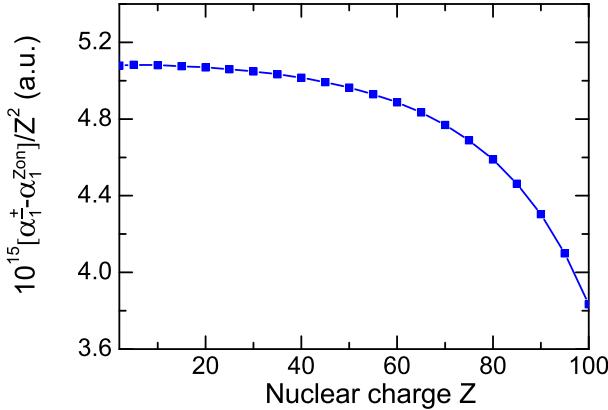


FIG. 4: (color online). Plot of  $10^{15}(\alpha_1^\pm - \alpha_1^{\text{zon}})/Z^2$  as a function of nuclear charge,  $Z$ .

Expressions for  $\alpha_1^\pm$  giving terms to  $O(\alpha^4 Z^4)$  [9],  $O(\alpha^6 Z^6)$  [10] and to all orders [11] have been derived. The  $O(\alpha^4 Z^4)$  expression of Zon [9] is

$$\alpha_1^{\text{zon}} = \frac{9}{2Z^4} \left[ 1 - \frac{28}{27}(\alpha Z)^2 + \frac{31 + 2\pi^2}{432}(\alpha^4 Z^4) + \dots \right]. \quad (25)$$

Figure 4 plots  $10^{15}(\alpha_1^\pm - \alpha_1^{\text{zon}})/Z^2$  as a function of  $Z$ . The  $Z \rightarrow 0$  limit of this difference demonstrates that the present calculations are in agreement with the analytic expression to  $O(\alpha^4 Z^4)$ . This provides a mutual validation of the B-spline calculations and the analytic expressions.

Figure 5 plots  $10^9 Z^4 \Delta\alpha_3$  as a function of  $Z$ . These are seen to go to a constant value as  $Z \rightarrow 0$ . By an analysis similar to that performed for the dipole polarizability, one can deduce that  $\alpha_3^\pm$ ,  $\alpha_3^+$ , and  $\alpha_3^K$  are equal to order  $O(\alpha^2 Z^2)$ . The different  $Z \rightarrow 0$  asymptotes for  $\Delta\alpha_3^\pm$  and  $\Delta\alpha_3^+$  indicate that  $O(\alpha^4 Z^4)$  terms are different for  $\alpha_3^\pm$  and  $\alpha_3^+$ .

The analysis demonstrating that the differences between  $\alpha_2^\pm$  and  $\alpha_2^+$  only appear at  $O(\alpha^4 Z^4)$  has already been reported [6]. It has previously been shown that these polarizabilities are agreement with the Kaneko  $O(\alpha^2 Z^2)$  [6]. It is also possible to plot  $10^9 Z^6 \Delta\alpha_4$  as a function of  $Z$  giving plots similar to Figs. 3 and 5. This demonstrates that  $\alpha_4^\pm$  and  $\alpha_4^+$  agree with  $\alpha_4^K$  at the  $O(\alpha^2 Z^2)$  level and the difference between  $\alpha_4^\pm$  and  $\alpha_4^+$  occurs at the  $O(\alpha^4 Z^4)$  order.

### C. Sum-rules for the hydrogen isoelectronic series

The non-relativistic TRK sum-rule,  $S_1(0)$  gives a value of unity [30, 33, 37] for all hydrogen-like atoms and ions. However,  $S_1^\pm(0)$  is exactly zero while the sum-rule,  $S_1^+(0)$

TABLE V: Relativistic multipole polarizabilities (in a.u.) for the ground states of the hydrogen isoelectronic series. All the figures listed are accurate. The notation  $a[b]$  means  $a \times 10^b$ .

$Z$	$\alpha_2^\pm$	$\alpha_3^\pm$	$\alpha_4^\pm$
1	14.998 829 822 856 441 699	131.237 821 447 844 662	2126.028 674 499 128 83
2	0.234 301 867 935 791 210 0	0.512 505 037 523 770 47	2.075 551 5460 612 051 9
5	9.581 285 372 324 0453 92[-4]	3.352 210 608 787 016 2[-4]	2.171 618 426 945 541 1[-4]
10	1.488 319 383 913 411 04[-5]	1.300 352 899 787 624[-6]	2.104 187 645 750 314[-7]
15	1.293 852 351 688 892 4[-6]	5.014 877 480 967 07[-8]	3.601 503 954 501 5[-9]
20	2.271 146 583 050 793[-7]	4.938 640 072 269 2[-9]	1.991 062 443 017[-10]
25	5.847 845 585 737 33[-8]	8.110 859 162 392[-10]	2.087 370 771 99[-11]
30	1.915 515 761 865 58[-8]	1.837 296 630 650[-10]	3.273 123 521 7[-12]
35	7.397 473 245 589 1[-9]	5.186 973 978 69[-11]	6.763 105 560[-13]
40	3.218 326 876 369 0[-9]	1.717 671 116 72[-11]	1.707 067 337[-13]
45	1.531 561 509 916 7[-9]	6.415 324 043 1[-12]	5.011 809 33[-14]
50	7.812 859 401 235[-10]	2.630 602 571 9[-12]	1.654 931 37[-14]
55	4.210 472 655 409[-10]	1.161 555 467 5[-12]	5.999 556 2[-15]
60	2.371 147 053 044[-10]	5.443 579 080[-13]	2.345 208 2[-15]
65	1.383 617 655 412[-10]	2.677 457 400[-13]	9.748 095[-16]
70	8.309 087 512 23[-11]	1.369 821 733[-13]	4.261 037[-16]
75	5.106 469 950 92[-11]	7.235 969 19[-14]	1.940 914[-16]
80	3.196 013 748 39[-11]	3.921 694 89[-14]	9.141 67[-17]
85	2.028 253 121 49[-11]	2.168 463 36[-14]	4.421 83[-17]
90	1.299 794 490 85[-11]	1.216 900 77[-14]	2.182 71[-17]
95	8.376 878 675 0[-12]	6.895 117 0[-15]	1.092 81[-17]
100	5.405 559 183 5[-12]	3.923 335 2[-15]	5.514 2[-18]

is almost equal to 1. The appropriate method to choose for the evaluation of the TRK sum rule has generated considerable discussion [12, 35, 36, 38–43]. Table VI compares the present B-spline values of  $S_1^+(0)$  and compares them against the earlier calculation of Drake and Goldman [12]. Keeping in mind the limited precision of the earlier calculation, the agreement with the Drake and Goldman calculation is perfect.

Figure 6 shows

$$\Delta S_1(0) = S_1^+(0) - S_1^{+\text{Levinger}}(0), \quad (26)$$

plotted as a function of  $Z$ . It is noticed that  $\Delta S_1(0)/Z^4$  goes to a constant as  $Z \rightarrow 0$ . This demonstrates that the present  $S_1^+(0)$  is in agreement with the expression of Levinger to order  $O(\alpha^2 Z^2)$ . It also demonstrates that the next term in the expression for  $S_1^+(0)$  occurs at the  $O(\alpha^4 Z^4)$  level. The near linear behaviour of  $\Delta S_1(0)/Z^4$  at small  $Z$  indicates that the expansion for  $S_1^+(0)$  contains a term of  $O(\alpha^5 Z^5)$ .

While the B-spline calculations of  $S_1^+(0)$  are compatible with  $O(\alpha^2 Z^2)$  expressions [35, 36], they cannot be reconciled with the  $O(\alpha^4 Z^4)$  expression of Cohen. A simple analysis near  $Z = 0$  suggests that

$$S_1^+(0) \approx 1 - \frac{5\alpha^2 Z^2}{6} + 2.71 \alpha^4 Z^4 - 6\alpha^5 Z^5 + O(\alpha^6 Z^6). \quad (27)$$

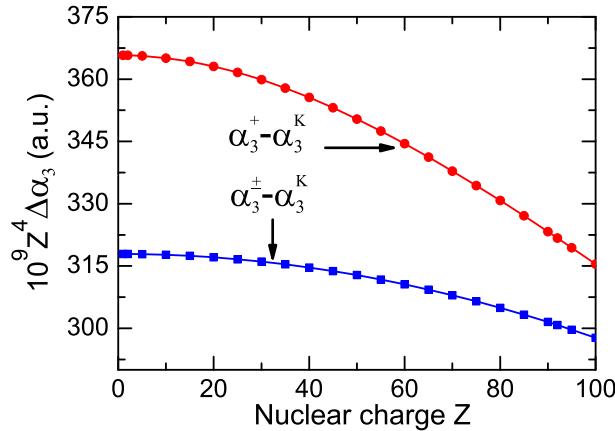


FIG. 5: (color online). Plot of  $10^9 Z^4 \Delta \alpha_3$  as a function of nuclear charge,  $Z$ .

TABLE VI: Comparison of the  $S_1^+(0)$  sum rules. All digits are stable with respect to further enlargement of the B-spline basis.

$Z$	Present	Ref. [12]
1	0.999 955 631 350 807	0.999 9556
2	0.999 822 612 102 297	
5	0.998 894 823 187 627	
10	0.995 622 481 263 678	0.995 62
15	0.990 287 581 618 103	
20	0.983 023 671 163 131	0.9830
25	0.973 973 703 862 452	
30	0.963 278 628 607 378	0.9633
35	0.951 070 787 251 835	
40	0.937 470 188 595 043	0.9375
45	0.922 582 481 520 977	
50	0.906 497 887 620 449	0.9065
60	0.871 018 387 592 671	0.8710
70	0.831 424 017 561 149	0.8314
80	0.787 815 483 542 815	0.7878
90	0.739 933 345 752 064	0.7399
100	0.686 987 401 548 771	0.69

It has not been possible to reconcile the coefficient of 2.71 with Eq. (8) of Cohen [36]. But it is unclear how to interpret  $\langle p^4 \rangle$  of Eq. (8) in [36]. The plot of  $S_1^+(0)$  depicted in Fig. 3 of [36] is certainly compatible with the present B-spline calculation. However, Fig. 3 of [36] plots the  $O(\langle p^2 \rangle)$  approximation to  $S_1^+(0)$  and this is certainly not equal to  $1 - \frac{5\alpha^2 Z^2}{6}$ .

Figure 7 shows the difference

$$\Delta S_1(n) = S_1^\pm(n) - S_1^+(n) , \quad (28)$$

plotted against  $Z$  for  $n = -1$  and  $n = -3$ . It is noticed that  $\lim_{Z \rightarrow 0} \Delta S_1(-1)$  and  $\Delta S_1(-3)$

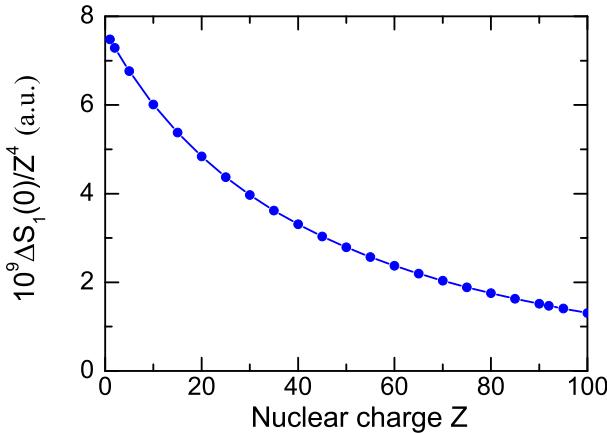


FIG. 6: (color online). Plots of  $10^9 \Delta S_1(0)/Z^4$  versus nuclear charge,  $Z$ .

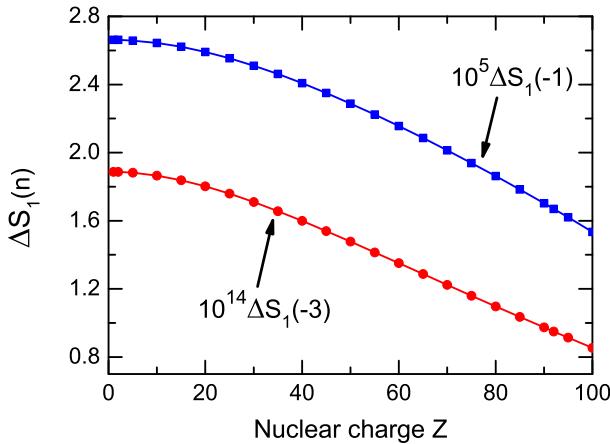


FIG. 7: (color online). Plots of  $\Delta S_1(-1)$  and  $\Delta S_1(-3)$  versus nuclear charge,  $Z$ .

both go to a constant as  $Z \rightarrow 0$ . Figure 3 established that  $\Delta S_1(-2)$  also has the same  $Z \rightarrow 0$  limiting behaviour. Writing either of the  $S_1(n)$  in the form

$$S_1(n) = S_1^{\text{NR}}(n) (1 + c_2 \alpha^2 Z^2 + c_4 \alpha^4 Z^4 + \dots), \quad (29)$$

allows one to deduce that the  $c_2$  coefficients are different for  $S_1^\pm(-1)$  and  $S_1^+(-1)$  since  $S_1^{\text{NR}}(-1) = 2/Z^2$ . However, one deduces that the  $c_2$  and  $c_4$  coefficients are actually the same for  $S_1^\pm(-3)$  and  $S_1^+(-3)$  since  $S_1^{\text{NR}}(-3) = 43/(4Z^6)$ .

#### D. Analytic expressions for the multipole polarizabilities of hydrogen-like ions

Analytic expressions were derived for  $\alpha_\ell^\pm$  by performing a least squares fit of the polarizabilities to Eq. (20). The polarizabilities were divided by the non-relativistic values prior to the fit. The value of  $\lambda_2$  was fixed at the values of Kaneko for  $\ell = 1, 2$  and 3. The  $\lambda_2$  value for  $\ell = 4$  was determined by evaluating Eq. (36) of Ref. [7]. The value of  $\lambda_4$  for  $\alpha_1^\pm$  was set to the value from Zon [9]. Table VII lists the numerical values of  $\lambda_{2i}$  coming from the

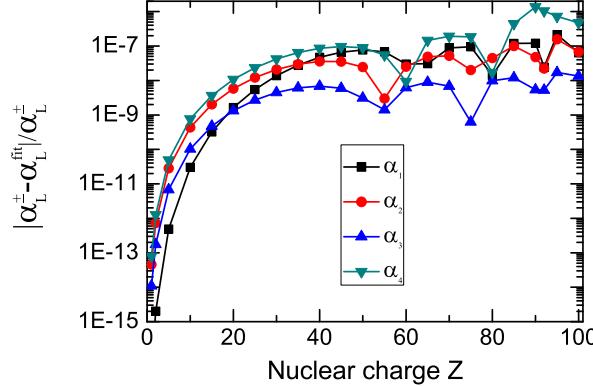


FIG. 8: (color online). Relative difference between  $\alpha_\ell^\pm$  and the fits to this using Eq. (20) as a function of nuclear charge,  $Z$ .

TABLE VII: The Eq. (20) fits to the multipole polarizabilities of hydrogen isoelectronic series ground states.

Term	$\alpha_1^\pm$ [13]	$\alpha_1^\pm$	$\alpha_2^\pm$	$\alpha_3^\pm$	$\alpha_4^\pm$
$\alpha^{\text{NR}}$	$\frac{9}{2Z^4}$	$\frac{9}{2Z^4}$	$\frac{15}{Z^6}$	$\frac{525}{4Z^8}$	$\frac{8505}{4Z^{10}}$
$\lambda_2$	$-\frac{28}{27}$	$-\frac{28}{27}$	$-\frac{879}{600}$	$-\frac{5123}{2940}$	$-\frac{33251}{17010}$
$\lambda_4$	0.117 451 87(1)	0.117 451 870 668 402	0.502 471 315	0.854 144 263	1.177 235 432
$\lambda_6$	0.007 482(1)	0.007 692 784	-0.014 151 521	-0.102 874 518	-0.228 232 960
$\lambda_8$	0.0010(1)	-0.003 271 333	0.002 052 103	0.001 434 636	0.011 629 938
$\lambda_{10}$	—	0.006 117 861	-0.000 261 805	0.001 019 239	-0.000 189 306
$\lambda_{12}$	—	-0.013 528 604	—	—	—
	$\alpha_1^+$	$\alpha_2^+$	$\alpha_3^+$	$\alpha_4^+$	
$\lambda_2$	$-\frac{28}{27}$	$-\frac{879}{600}$	$-\frac{5123}{2940}$	$-\frac{33251}{17010}$	
$\lambda_4$	—	0.171 953 291	0.601 241 304	0.981 404 521	1.323 923 421
$\lambda_6$	—	-0.069 671 936	-0.164 544 588	-0.321 798 414	-0.506 146 068
$\lambda_8$	—	0.075 248 612	0.118 942 451	0.171 613 014	0.236 007 349
$\lambda_{10}$	—	-0.051 443 668	-0.057 448 561	0.073 735 494	-0.093 122 365

fit. These coefficients give a more precise representation of the exact dipole polarizabilities than two previous representations [12, 13]. The expressions for the quadrupole and octupole polarizabilities are novel.

The quality of the fit to the B-spline  $\alpha_\ell^\pm$  can be seen from Fig. 8. The quality of the fits are of very high accuracy at the smaller values of  $Z$ . This occurs since the leading  $\lambda_2 \alpha^2 Z^2$  term uses the exact value of  $\lambda_2$ . The quality of the fit is degraded at larger values of  $Z$ . However, the maximum relative error in the analytic expressions only exceeds one part per million for values of  $Z$  close to 100.

Equation (20) was also used to create an analytic expression for  $\alpha_\ell^+$ . In this case, the  $\lambda_{2i}$

TABLE VIII: The second-order dispersion coefficients (in a.u.) for the H(1s)-H(1s) and H(1s)-He<sup>+</sup>(1s) systems. Results are given for the sum rules evaluated with and without the states of the Dirac sea. All tabulated digits are accurate. The notation  $a[b]$  means  $a \times 10^b$ .

	$C_n^+$	$C_n^\pm$	Non-relativistic
H(1s)-H(1s)			
$C_6$	6.498 392 250 007 09	6.498 392 245 754 06	6.499 026 705 405 84
$C_8$	1.243 840 307 694 35[2]	1.243 840 306 577 93[2]	1.243 990 835 836 22[2]
$C_{10}$	3.285 370 791 861 60[3]	3.285 370 788 289 10[3]	3.285 828 414 967 42[3]
H(1s)-He <sup>+</sup> (1s)			
$C_6$	0.657 548 755 759 311	0.657 548 758 416 787	0.657 716 656 238 770
$C_8$	8.335 406 342 724 22	8.335 406 384 081 09	8.337 819 589 166 31
$C_{10}$	1.588 773 716 759 79[2]	1.588 773 725 479 53[2]	1.589 267 575 526 71[2]

parameters with  $i > 1$  were treated as fitting parameters. The results of the fit are tabulated in Table VII.

#### IV. DISPERSION COEFFICIENTS

The long-range dispersion interaction between two spherically symmetric atoms can be written

$$V_{\text{disp}}(R) \sim - \sum_{n=3}^{\infty} \frac{C_{2n}}{R^{2n}}, \quad (30)$$

The dispersion coefficients,  $C_{2n}$  can be evaluated using oscillator strength sum rules. The explicit expression is

$$\begin{aligned} C_{2n} = & \sum_{\ell_i=1}^{n-2} \sum_{\ell_j=1}^{n-2} \delta_{n-1, \ell_i + \ell_j} \frac{(2n-2)!}{4(2\ell_i)!(2\ell_j)!} \\ & \times \sum_{ij} \frac{f_{A,gi}^{(\ell_i)} f_{B,gj}^{(\ell_j)}}{\varepsilon_{A,gi} \varepsilon_{B,gj} (\varepsilon_{A,gi} + \varepsilon_{B,gj})}, \end{aligned} \quad (31)$$

where  $\ell_i + \ell_j + 1 = n$  and  $\varepsilon_{A,gi}$  is the excitation energy from state  $g$  to state  $i$  for atom  $A$ . The sum implicitly includes the continuum, and  $f_{A,gi}^{(\ell_i)}$  is the oscillator strength of multipole  $\ell_i$  connecting the state  $g$  to the excited state  $i$  for atom  $A$ . Considerations of molecular symmetry do not have a direct effect on Eq. (31) when both atoms are in spherically symmetric states.

It is surprising that there has not yet been any calculation of the hydrogen dimer dispersion coefficients based on oscillator strengths from the Dirac equation. This is rectified in Table VIII where the  $C_6$ ,  $C_8$  and  $C_{10}$  coefficients are given for two hydrogen atoms in their ground states. Table VIII also gives the dispersion coefficients between a hydrogen atom and a He<sup>+</sup> ion.

The use of the Dirac equation leads to the H-H  $C_6$  being reduced by 0.00063 a.u. or 0.0098%. The relative difference is about twice as large as the difference between the rela-

tivistic and non-relativistic polarizabilities. The reduction in the size of  $C_6$  is larger for the H-He<sup>+</sup> system, being about 0.026%.

## V. CONCLUSIONS

A computational investigation based on B-spline methods has been used to investigate the polarizabilities and related sum rules of the hydrogen isoelectronic series. Dipole polarizabilities have been computed to a higher precision than any previous calculations. One distinction with previous calculations is that results were also reported for calculations where the negative-energy Dirac sea is excluded from the intermediate sum. The agreement with previously derived analytic expressions [7, 9, 10] for the dipole polarizability could not be better. High precision calculations of the multipole polarizabilities for  $\ell = 2, 3, 4$  are also given. The present results provided a computational validation of the earlier works of Kaneko [7] and Zon [9]. The  $\alpha_\ell^\pm$  polarizabilities are in agreement with the Kaneko expressions at the  $O(\alpha^2 Z^2)$  level. The  $\alpha_1^\pm$  polarizability is also in agreement with the expressions of Zon [9], which includes terms at the  $O(\alpha^4 Z^4)$  level.

Precise values for other oscillator strength sum rules have also been computed. The sum-rule  $S_\ell^\pm(0) = \sum_i f_{gi}^{(\ell)} = 0$  provides a valuable check of the numerical reliability of the calculations. The sum-rule,  $S_1^+(0)$  has been shown to be compatible with the  $O(\alpha^2 Z^2)$  expression of Levinger *et al* [35]. It is also compatible with earlier numerical calculations [12, 36].

One aspect of the present work that represents a departure from earlier work has been the treatment of the states of the negative energy sea. Existing practice is that calculations of polarizabilities include the states of the negative energy sea, while calculations of the Bethe sum rule tend to omit these state. The philosophy of the present work has simply been to do two calculations for most properties, those that include the states of the Dirac Sea and those that omit them.

Analytic expressions for  $\alpha_\ell^\pm$  and  $\alpha_\ell^+$  to relative precisions not exceeding  $10^{-6}$  have been obtained by fitting an  $(\alpha Z)^n$  expansion to the computed polarizabilities. The  $C_6$ ,  $C_8$  and  $C_{10}$  dispersion coefficients for the long-range H-H and H-He<sup>+</sup> interactions were also computed.

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